CHIMIESOLYMPIAD
LËTZEBUERG 2020

SEMI-FINALS : Problems

Dear students,

We congratulate you for your participation in the Chemistry Olympiad and we wish you lots of success in this second round as well as in your studies and in all of your future endeavours. We also congratulate you for having succeeded in the first round, which has enabled you to tackle the "Problems" round today. **Before undertaking this next round, please carefully read the following instructions.**

Attached you will find 4 questions. The subjects of these questions are: general chemistry, stoichiometry, redox and organic chemistry.

You have **two hours** to answer these questions. You can use a non-programmable calculator, but you cannot have any personal documents on you.

Include your name and your institution's name at the start of **each** question. Write your answers to each of the questions on the question paper (front and back, if necessary). **Clearly indicate your reasoning and your calculations. Justify your answers and indicate the units in the final answers.** The last page is a draft sheet which will not be taking into account for the final assessment. Detach the two first pages and keep them for reference.

Following the results of this second round, the 12 best students will be invited to participate in a final (practical) round, which will take place on **Saturday 25th April 2020 at 09h00 at the University of Luxembourg's Limpertsberg laboratories**. This final round will determine the 4 laureates of the national Chemistry Olympiad, and will also constitute the Luxembourg team for the 52nd IChO in Istanbul, from the 6th to the 15th of July 2020. For more information please see http://icho.olympiades.lu/.

The results of this second round will be taken into account for the ranking of the four finalists !!!

Best wishes and good luck.
The Chemistry Olympiad organisers

Detach this sheet and keep it for information.

Useful Constants

(Detach this page if necessary)

LIÈGE université **TABLEAU PÉRIODIQUE DES ÉLÉMENTS**

masse atomique relative A_r — élément X — nombre atomique Z

1 I a			3 III b	4 IVb	5 V b	6 VI b	7 VII b	8	9	10 VIII b	11 I b	12 II b	13 III a	14 IV a	15 V a	16 VI a	17 VII a	18 VIII a
1,01 H 1	2 II a																	4,00 He 2
6,94 Li 3	9,01 Be 4												10,81 B 5	12,01 C 6	14,01 N 7	16,00 O 8	19,00 F 9	20,18 Ne 10
22,99 Na 11	24,31 Mg 12												26,98 Al 13	28,09 Si 14	30,97 P 15	32,07 S 16	35,45 Cl 17	39,95 Ar 18
39,10 K 19	40,08 Ca 20		44,96 Sc 21	47,88 Ti 22	50,94 V 23	52,00 Cr 24	54,94 Mn 25	55,85 Fe 26	58,93 Co 27	58,69 Ni 28	63,55 Cu 29	65,39 Zn 30	69,72 Ga 31	72,61 Ge 32	74,92 As 33	78,96 Se 34	79,90 Br 35	83,80 Kr 36
85,47 Rb 37	87,62 Sr 38		88,91 Y 39	91,22 Zr 40	92,91 Nb 41	95,94 Mo 42	Tc* 43	101,07 Ru 44	102,91 Rh 45	106,42 Pd 46	107,87 Ag 47	112,41 Cd 48	114,82 In 49	118,71 Sn 50	121,75 Sb 51	127,60 Te 52	126,90 I 53	131,29 Xe 54
132,91 Cs 55	137,33 Ba 56	(1) 57 - 70	174,97 Lu 71	178,49 Hf 72	180,95 Ta 73	183,9 W 74	186,21 Re 75	190,21 Os 76	192,22 Ir 77	195,08 Pt 78	196,97 Au 79	200,59 Hg 80	204,38 Tl 81	207,21 Pb 82	208,98 Bi 83	Po* 84	At* 85	Rn* 86
Fr* 87	Ra* 88	(2) 89 - 102	Lr* 103	Rf* 104	Db* 105	Sg* 106	Bh* 107	Hs* 108	Mt* 109	Ds* 110	Rg* 111	Cn* 112	Nh* 113	Fl* 114	Mc* 115	Lv* 116	Ts* 117	Og* 118

1) Lanthanides	138,92 La 57	140,12 Ce 58	140,91 Pr 59	144,24 Nd 60	Pm* 61	150,36 Sm 62	151,97 Eu 63	157,25 Gd 64	158,93 Tb 65	162,50 Dy 66	164,93 Ho 67	167,26 Er 68	168,93 Tm 69	173,04 Yb 70
2) Actinides	Ac* 89	232,04 Th 90	231,04 Pa 91	238,03 U 92	Np* 93	Pu* 94	Am* 95	Cm* 96	Bk* 97	Cf* 98	Es* 99	Fm* 100	Md* 101	No* 102

Constants

$R = 8{,}31$ J·mol^{-1}·K^{-1} $\qquad 1F = 9{,}65 \cdot 10^{4}$ C·mol^{-1}

$R = 8{,}21 \cdot 10^{-2}$ L·atm·mol^{-1}·K^{-1} $\qquad N_A = 6{,}02 \cdot 10^{23}$ mol^{-1}

Volume of an ideal gas mole at 273 K and 101 325 Pa : 22,4 dm^3·mol^{-1} (L·mol^{-1})

Simplified pH formulas :

Strong acid	Weak acid	Strong base	Weak base
$pH = -\log c_{acid}$	$pH = \frac{1}{2}(pK_a - \log c_{acid})$	$pH = 14 + \log c_{base}$	$pH = 14 - \frac{1}{2}(pK_B - \log c_{base})$

Buffer mix : $pH = pK_a + \log \frac{c_{base}}{c_{acid}}$ $\qquad$ At 25 °C : $K_w = K_{H_2O} = [H_3O^+]\cdot[OH^-] = 1{,}0\cdot10^{-14}$

SURNAME : _____

Name : _____

Institution : _____

Question I : Ammonium salts

1a	1b	1c	1d	Total Question I
3	4	3	20	30

A solid is composed of three crystallised ammonium salts: chloride, sulphate and nitrate.

We do not know the quantitative composition of this sample and, in order to determine it, the following tests are carried out on three samples of equal mass:

- The first sample is heated in the presence of an aqueous solution of concentrated potassium hydroxide. The gas given off is captured in 100,0 mL of an aqueous solution of hydrogen chloride (hydrochloric acid) with a concentration of $2{,}00 \cdot 10^{-1}$ mol/L. The excess acid is titrated by 41,20 mL of a sodium hydroxide solution with a concentration of $9{,}87 \cdot 10^{-2}$ mol/L.

- The second sample is heated in the presence of an excess of metallic zinc in an aqueous solution of concentrated potassium hydroxide. The nitrate anions react with the zinc to form ammonia and zincate ions $Zn(OH)_3^-$. The gas formed is absorbed in 100,0 mL of an aqueous solution of hydrochloric acid with a concentration of $2{,}00 \cdot 10^{-1}$ mol/L. The excess is titrated by 32,15 mL of an aqueous solution of sodium hydroxide with a concentration of $9{,}87 \cdot 10^{-2}$ mol/L.

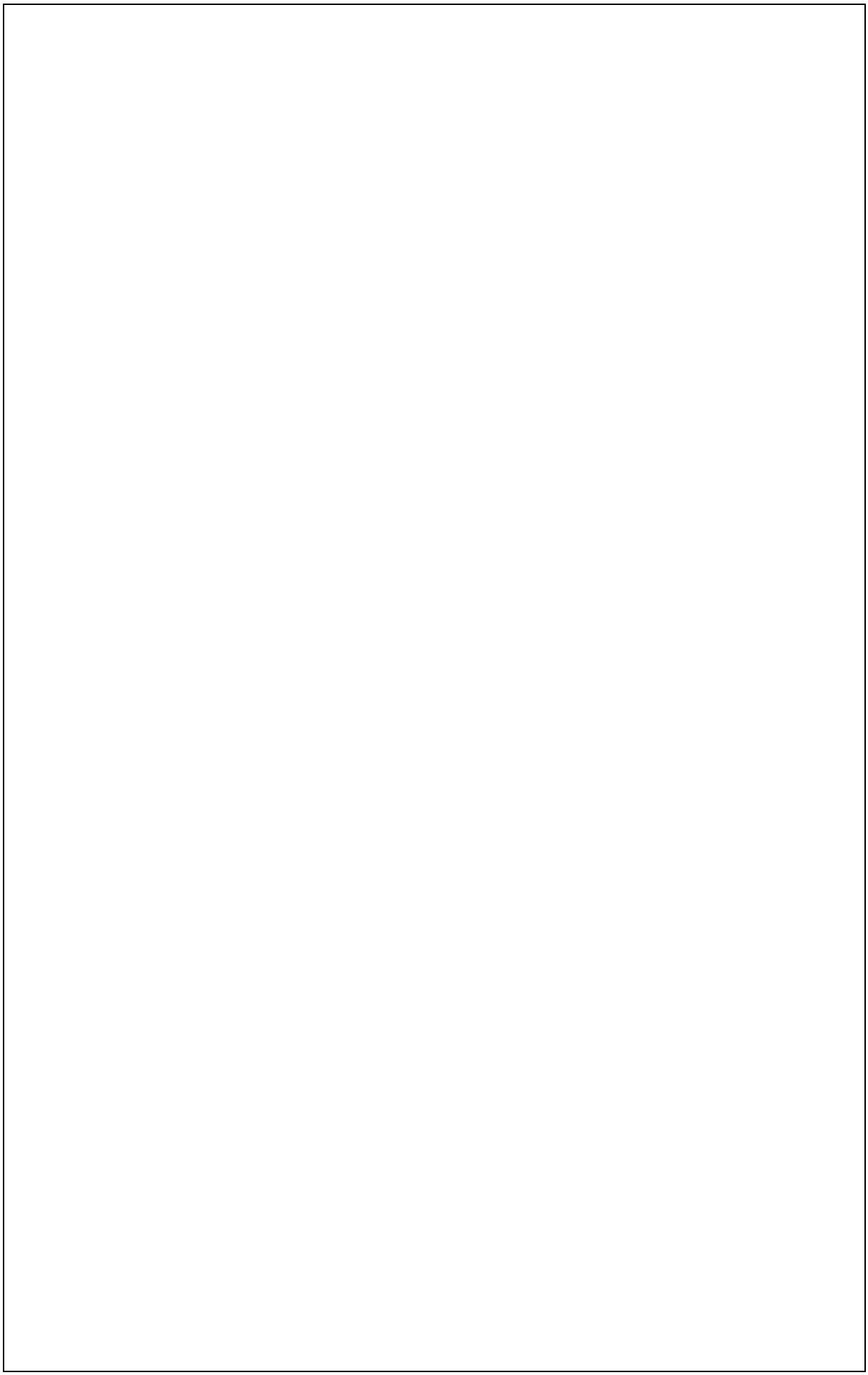
- The third sample is treated with an excess of an aqueous solution of barium chloride. The mass of the precipitate after filtration and drying is 0,02334 g.

a) Write out all of the equations corresponding to the chemical reactions taking place in the first sample.

b) Balance the equation corresponding to the reaction taking place between the nitrate ions and the metallic zinc in the second sample.

c) Balance the equation corresponding to the reaction taking place during the third sample.

d) Calculate the mass and the mass percentage of each of the three ammonium salts in the original sample.



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale,
de l'Enfance et de la Jeunesse

ACLg

UNIVERSITÉ DU
LUXEMBOURG

Fonds National de la
Recherche Luxembourg

CHAMBRE DE
COMMERCE
LUXEMBOURG

CHAMBRE DES SALARIES
LUXEMBOURG

andré losch
fondatioun

SURNAME : _____

Name : _____

Institution : _____

Question II : Hydroxyapatite

2a	2b	2c	2d	2e	2f	2g	Total Question II
3	5	2	5	6	3	5	29

Human bone is mostly composed of hydroxyapatite $Ca_5(PO_4)_3(OH)$. In situations of bone disease or fracture, grafts of synthetic hydroxyapatite are possible. These can be obtained by the precipitation of calcium hydroxide and phosphoric acid.

a) Write out the balanced equation of this reaction.

A bone containing 100 g of hydroxyapatite is needed to perform a graft on a patient with hip dysplasia.

b) Calculate the calcium hydroxide mass and the volume of phosphoric acid 2M needed to precipitate the necessary hydroxyapatite.

In order to convert the hydroxyapatite powder into a sufficiently dense piece, it must be heated to over 1000°C. However, the temperature cannot be too high since at 1100°C the hydroxyapatite will degrade according to the following unbalanced equation:

$$Ca_5(PO_4)_3(OH)_{(s)} \rightarrow Ca_3(PO_4)_{2(s)} + CaO_{(s)} + H_2O_{(g)}$$

c) Give the chemical name of the **two** solids produced by the reaction, as well as the common name of CaO.

The CaO content contained in the graft cannot exceed 5% in mass. To ensure this, it is possible to measure the pressure of the water vapour generated by the reaction.

d) In order to not exceed the maximum CaO content in the case of the implant of 100g, what is the maximum pressure (atm) of the water vapour in an oven of $1m^3$ at 1100°C?

To avoid calcium deficiencies, it is recommended to consume dairy products.

e) Given that a human bone is composed of 65% hydroxyapatite, 25% of organic matter and 10% water, and that a 250 mL glass of milk (volumic mass = 1,032 g/cm^3) contains 300 mg of calcium, how many litres of milk would need to be drunk to obtain the equivalent calcium content of an adult human skeleton (5kg) ?

In addition to hydroxyapatite, fluorapatite, $Ca_5(PO_4)_3F$, is contained in human teeth. It can be synthesised by using a double diffusion method with a gelatine membrane separating solutions containing ions of F^-, HPO_4^{2-} and Ca^{2+}. This synthesis creates a hybrid material of bioorganic polymer / inorganic phosphate, which resembles dental (or bony) tissue.

f) Give a reasonable composition of the two solutions on each side of the gelatine membrane that would allow for the preparation of fluorapatite as the key substance targeted in this double diffusion experiment. To do this, place a cross in the field(s) which correspond to the solutions 1 and 2.

	5 mM $Ca(NO_3)_2$	1 mM NaF	3 mM Na_2HPO_4
Solution 1			
Solution 2			

Osmotic pressure is a force determined by the difference in concentration between two solutions found on either side of a semi-permeable membrane.
This pressure is calculated using the following formula:

$$\pi = \Delta cRT$$

Where π is the osmotic pressure,
Δc is the difference of **total ion concentrations** between the two solutions,
R is the universal constant of perfect gases,
T is the temperature (in Kelvin).

g) Calculate the osmotic pressure acting on the membrane at the beginning of this experiment at a temperature of 25°C.

SURNAME : _____

Name : _____

Institution : _____

Question III : Bleach dosage

3a	3b	3c	Total Question III
4	5	7	16

Theory introduction

An oxidation reaction is a reaction during which a reactant gives up (or loses) one or more electrons. The oxidation number (or level of oxidation) of the reactant will therefore increase.

Example : $Cu \rightarrow Cu^{2+} + 2e^-$
Here, the copper goes from oxidation number 0 to +II.

A reduction reaction is a reaction during which a reactant captures (or takes) one or more electrons. The oxidation number (or level of oxidation) of the reactant will therefore decrease.

Example : $HNO_3 + 3e^- + 3\ H^+ \rightarrow NO + 2\ H_2O$
Here, the nitrogen goes from oxidation number +V to +II.

These reactions always take place in pairs to form a redox reaction. Based on the examples above, the redox reaction is :

$Cu \rightarrow Cu^{2+} + 2e$ | ·3
$HNO_3 + 3\ e^- + 3\ H^+ \rightarrow NO + 2\ H_2O$ | ·2

$3\ Cu + 2\ HNO_2 + \cancel{6e^-} + 6\ H^+ \rightarrow 3\ Cu^{2+} + \cancel{6e^-} + 2\ NO + 4\ H_2O$

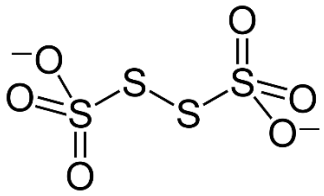
A solution **D**, obtained by diluting 25 cm^3 of the commercial bleach product JAVEL « LA CROIX » with 500 cm^3 of de-ionised water, this then undergoes serial dilution.

Principles of dilution

The active ingredient in commercial bleach is the hypochlorite anion ClO^-. During its reaction with an excess of potassium iodide in an acidic environment, the hypochlorite anion is reduced to a chloride anion with an equivalent quantity of iodine also created.

a) Show the oxidation and reduction equations, as well as the resulting redox equation of the reaction of the hypochlorite anion on the iodide anion by indicating the oxidation numbers of the oxidised and reduced atoms.

The quantity of iodine formed is then dosed by titration with a 0,05mol/L solution of sodium thiosulphate $Na_2S_2O_3$, which again reduces the iodine into an iodide anion. The thiosulphate is itself oxidised into a tetrathionate ion $S_4O_6^{2-}$ whose structure is :



b) Show the oxidation and reduction equations, as well as the resulting redox equation of the reaction of the thiosulphate anion on the iodine by indicating the oxidation numbers of the oxidised and reduced species.

A 10,0 cm^3 dose of the solution **D** (diluted bleach « LA CROIX ») mixed with a 10 cm^3 solution of potassium iodide at 0,1 mol/L and 10 cm^3 of sulphuric acid at 1 mol/L required 7,4cm^3 of sodium thiosulphate at 0,05 mol/L.

c) Calculate, in grams of sodium hypochlorite per litre of solution, the content of a non-diluted commercial solution of Javel LA CROIX.

SURNAME : _____

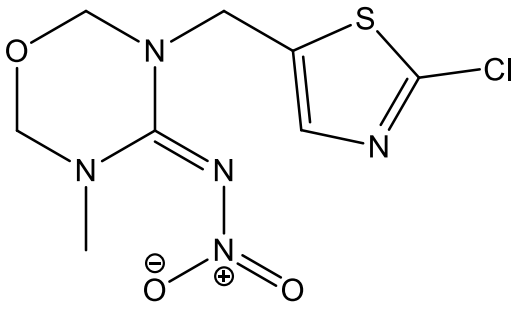
Name : _____

Institution : _____

Question IV : Bees and Brexit

4a	4b1	4b2	4b3	4b4	4c	4d	4e1	4e2	4f	4g	Total Question IV
2	2	2	2	2	2	2	3	3	2	3	25

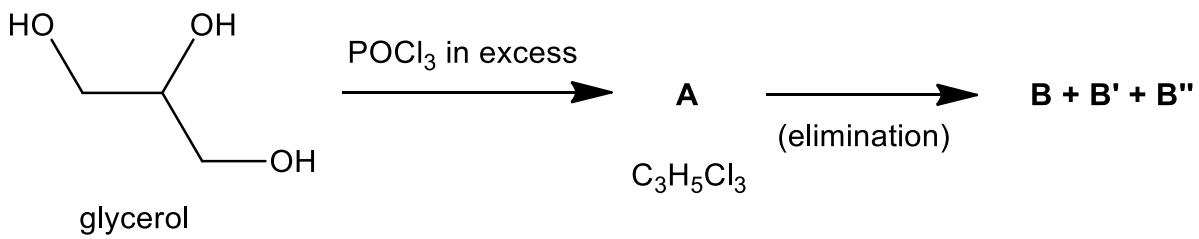
Pesticides belonging to the group of neonicotinoids are potentially toxic to bees. Thiamethoxam is one of the three neonicotinoids that the European Union has banned the use of in open air. Now that the United Kingdom has left the European Union, this pesticide can once again be used there, with potential catastrophic effects on the bee population.



Thiamethoxam

a) Give the molecular formula of Thiamethoxam.

The synthesis of Thiamethoxam begins with glycerol. During the conversion of **A** into **B**, two other by-products (**B'** and **B"**) can be formed. **B**, **B'** and **B"** are isomers. **B'** and **B''** are configurational isomers and they form **B'** much more frequently than **B"**.



b) Draw the structures of **A**, **B**, **B'** and **B''**.

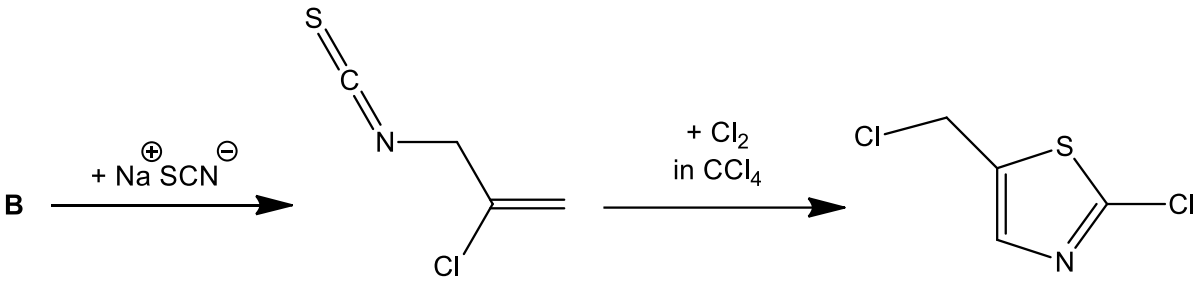
A

B

B'

B''

B reacts with sodium thiocyanate (NaSCN) to form **C**, which can be converted into **D** by a reaction with chlorine and tetrachloromethane.



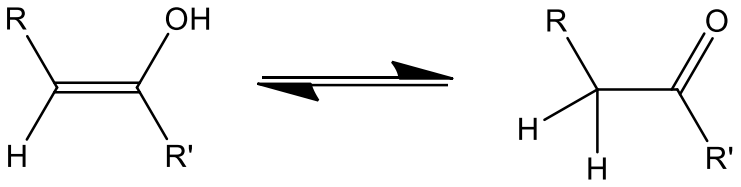
C **D**

c) Draw the resonance structure of the thiocyanate ion which explains the formation of **C**.

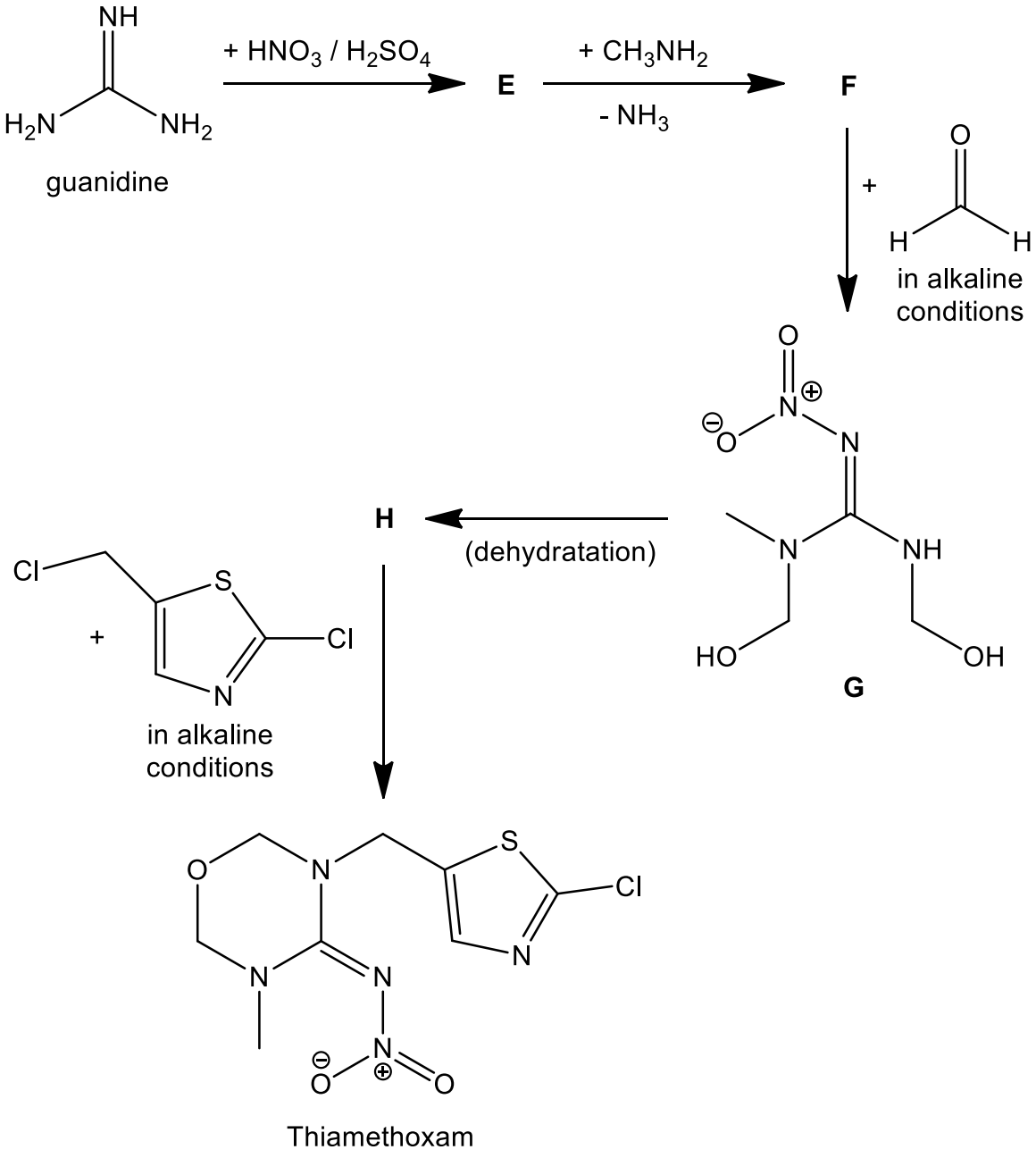
The rest of the synthesis begins with guanidine.

Several tautomers of guanidine exist, which all interconvert very rapidly into a stable form. Tautomers are pairs of constitutional isomers, which are solely differentiated by the position of the hydrogen atoms and the double bonds.

e.g.:



Several tautomers of each intermediate exist (**E**, **F**, **G** et **H**).



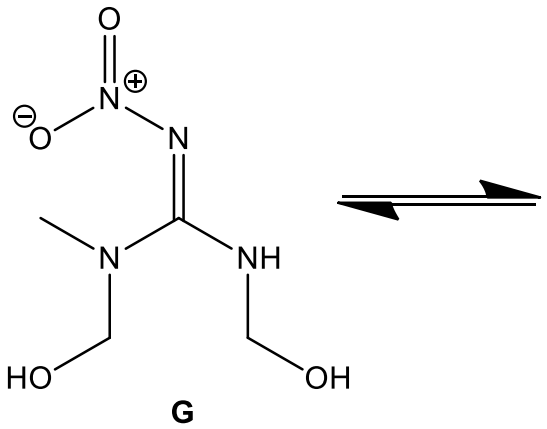
d) Draw the electrophile that reacts with guanidine to form **E**, by clearly indicating its geometry.

e) Draw the structures of **E** and **F**. It's enough to draw one tautomer for each compound.

E

F

f) Draw a tautomer of **G**.



G

g) Draw the structure of **H**. It's enough to draw one tautomer.

H